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(57) Abstract

Blended polymer compositions are described which comprise (A) an olefin polymer, (B) at least one second polymer having a glass transition temperature greater than the glass transition temperature of olefin polymer (A) such as: copolymers and terpolymers of styrene and maleic anhydride or a maleimide; polystyrene blended with a polyarylene ether, and optionally an elastomer; blends or reaction products of styrene-maleic anhydride or maleimide copolymers or terpolymers with elastomers; polycarbonates, etc., and (C) at least one compatibilizing agent selected from the group consisting of various block copolymers of vinyl aromatic compounds and conjugated dienes, and their partially hydrogenated derivatives. The blended polymer compositions of the present invention can be extruded, coextruded, thermoformed, blow-molded, injection-molded, compression-molded, calendered, laminated, foamed, stamped, pultruded, or extrusion die coated onto a continuous fiber to form shaped articles useful in a variety of applications. The compatibilized and blended polymer compositions of the present invention exhibit excellent heat distortion properties as well as excellent strength, toughness, stiffness, gloss, ease of processing and forming, improved filler interaction, hardness, adherability and shrinkage characteristics and they are retortable and microwaveable.

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POLYMER COMPOSITIONS COMPATIBILIZED WITH STYRENE BLOCK COPOLYMERS AND ARTICLES PRODUCED THEREFROM

Cross-Reference to Related Application

This application is a continuation-in-part application of pending Application Serial No. 07/271,978 filed on November 15, 1988, and the disclosure and claims of said application are hereby incorporated by reference in their entirety.

Background of the Invention

Field of the Invention

This invention relates generally to compatibilizing two or more incompatible polymer systems. The invention also relates to compounded, compatibilized polyolefin-styrene copolymer or polymeric blend compositions and articles of manufacture produced therefrom.

State of the Art

Polymeric blends have been known for years. Typically, blends of polymers result in a material which combines the poorest properties of the constituents. This is a result of the incompatibility of the constituent polymers resulting in little, if any, adhesion at the interface between the different constituent polymers. Furthermore, this incompatibility stems in part from the structure of the individual polymers. Thermodynamically, one polymeric phase has more of an affinity for itself than for the other polymeric phase so that

intermolecular forces between the two polymers are weak. For example, a blend of a polar polymer and a non-polar polymer would result in an incompatible system demonstrating poor physical properties for lack of wetting and adhesion at the interface. Even in cases when the polarity of the polymers in a blend is similar, compatibility is generally not achieved because the entropy change upon mixing of high polymers is not favorable.

Such incompatibility problems may be overcome through the use of a compatibilizing agent. A compatibilizing agent is a material which, on a molecular scale, has particular regions which are compatible with each of the incompatible constituent polymers. Such compatibilizing agents typically surround one polymeric phase providing a chemical and/or physical bridge to the other polymeric phase. Insomuch as portions of the compatibilizing agent are compatible with each of the constituent polymers, the bonding between the two incompatible polymeric phases is effectively enhanced through this intermediate compatibilizing phase. Such a system of incompatible polymers coupled by a compatibilizing agent results in a material which advantageously combines the more desirable properties of the constituent polymers. Lindsey et al, J. Appl. Polymer Sci., Vol. 26, 1-8 (1981) describe a method of reclaiming mixed immiscible polymers by employing a compatibilizing agent. The system studied was a high density polyethylene (HDPE) and polystyrene (PS) and a styrene-ethylene-butene-1-styrene (SEBS) copolymer (a linear triblock copolymer) as the compatibilizing agent. These ternary blends exhibited a considerable improvement in the balance of mechanical properties over a binary blend of high density polyethylene and polystyrene.

Bartlett et al, Modern Plastics, Dec. 1981, 60-62 describes a system comprising polypropylene, polystyrene and styrene-ethylene-butene-1-styrene as a compatibilizer. This work focused on those parameters that affected the extent of the polypropylene crystallinity.

Polystyrene homopolymers and copolymers compatibilized with polyolefins have been available for several years. Furthermore, molded articles have been produced from such compatibilized polymer compositions. For example, U.S. Patent Nos. 4,386,187 and 4,386,188 disclose a thermoformable polymer blend of a polyolefin, a styrene polymer and styrenic diblock and triblock copolymer rubbers. While a number of styrene polymers and copolymers are disclosed, a copolymer of styrene and maleic anhydride is not.

U.S. Patent 4,647,509 discloses a multilayer thermoformable packaging material comprising a first layer of (a) a vinylidene chloride polymer, (b) an incompatible polymer, e.g., polyesters and nylons, and (c) a compatibilizing agent, and a second layer of (a) a blend of an olefin polymer, a styrenic polymer, and a compatibilizing polymer, and (b) scrap material produced from the first and second layers. The compatibilizing polymers for the second layer are preferably block copolymers of olefins and styrene such as copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, etc.

U.S. Patent 4,107,130 discloses a multicomponent polymer blend comprised of a polyolefin, a selectively hydrogenated monoalkenyl arene-diene block copolymer, and at least one dissimilar engineering thermoplastic resin.

Summary of the Invention

Blended polymer compositions are described which comprise (A) an olefin polymer, (B) at least one second polymer having a glass transition temperature greater than the glass transition temperature of olefin polymer (A) such as: copolymers and terpolymers of styrene and maleic anhydride or a maleimide; polystyrene blended with a polyarylene ether, and optionally an elastomer; blends or reaction products of styrene-maleic anhydride or maleimide copolymers or terpolymers with elastomers; polycarbonates, etc., and (C) at least one compatibilizing agent selected from the group consisting of various block copolymers of vinyl aromatic compounds and conjugated dienes and/or their partially hydrogenated derivatives.

The blended polymer compositions of the present invention can be extruded, coextruded, thermoformed, compression molded, blow-molded, injection-molded, calendered, laminated, stamped, pultruded, foamed, or extrusion die coated onto continuous fibers, to form shaped articles useful in a variety of applications. The compatibilized and blended polymer compositions of the present invention exhibit excellent heat distortion properties as well as excellent strength, toughness, stiffness, gloss, ease of processing, improved filler interaction, hardness, adherability and shrinkage characteristics, and they are retortable and microwaveable.

Description of the Preferred Embodiments

The novel blended polymer compositions of the present invention comprise a mixture of two or more polymers and a compatibilizing agent as described in more detail herein. An essential component of the blended polymer compositions of the present invention is at least one olefin polymer.

(A) The Olefin Polymers.

The olefin polymers employed in the blends of the present invention generally are semi-crystalline or crystallizable olefin polymers including homopolymers, copolymers, terpolymers, or mixtures thereof, etc., containing one or more monomeric units. Polymers of alpha-olefins or 1-olefins are preferred in the present invention, and these alpha-olefins may contain from 2 to about 20 carbon atoms. Alpha-olefins containing 2 to about 6 carbon atoms are preferred. Thus, the olefin polymers may be derived from olefins such as ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, 4-ethyl-1-hexene, etc. Examples of particularly useful olefin polymers include low-density polyethylene, high-density polyethylene, linear low density polyethylene, ultra low density polyethylene, polypropylene, (high and low density) poly(1-butene), ultra low molecular weight polyethylene, ethylene-based ionomers, poly(4-methyl-1-pentene), ethylene-propylene copolymers, ethylene-propylene-diene copolymers (EPDM) copolymers of ethylene and/or propylene with other copolymerizable monomers such as ethylene-1-butylene copolymer, ethylene-vinyl acrylate copolymer, ethylene-ethyl acetate copolymer, propylene-4-methyl-1-pentene copolymer, ethylene-vinyl acetate, ethylene vinyl alcohol, ethylene-methyl acrylate-acrylic acid terpolymers, etc. Halogenated olefins, polymers and copolymers may also be used in this invention.

Olefin polymers having a semi-crystalline or crystallizable structure are particularly useful in the present invention since such polymers are capable of forming a continuous structure with the other polymers in the polymer blend of the present invention. The

number average molecular weight of the polyolefins is preferably above about 10,000 and more preferably above about 50,000. In addition, it is preferred in one embodiment that the apparent crystalline melting point be above about 75°C and preferably between about 75°C and about 250°C. Most commercial polyethylenes have a number average molecular weight of from about 50,000 to about 500,000. The olefin polymers useful in preparing the polymer blends of the present invention are well-known to those skilled in the art and many are available commercially. The olefin polymers may be homopolymers, impact copolymers, block copolymers, random copolymers, thermoplastic olefinic elastomers (TPO), etc., or mixtures thereof. Polyethylene and polypropylene are preferred olefin polymers, and polypropylenes such as Himont's Profax 6523 (homopolymer) and Shell's 7C06 or Exxon's PD7132 or Aristich's 4040F (polypropylene-ethylene copolymers) are particularly preferred.

(B) <u>Higher Glass Transition Temperature Second Polymer</u>.

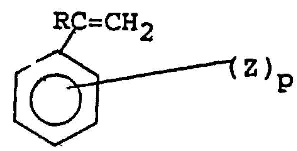
The second polymer in the blended polymer compositions of the present invention is at least one polymer having a glass transition temperature which is greater than the glass transition temperature of the olefin polymer (A). Generally, the glass transition temperature of the second polymer will be above about 75°C.

(B-1) <u>Copolymers of Vinyl Aromatic Compounds and Unsaturated Dicarboxylic Acid Anhydrides, Imides, Metal Salts, or Partial Esters of the Dicarboxylic Acids</u>.

A particularly preferred second polymer in the blended polymer compositions of the present invention is at least one copolymer of a vinyl aromatic compound and unsaturated dicarboxylic acid anhydrides, imides, metal salts and partial esters. Copolymers of a vinyl aroma-

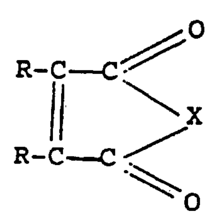
tic compound and maleic anhydride, N-substituted maleimide, metal salts or partial esters of maleic acid derivatives are particular examples.

The vinyl aromatic compounds include styrene and the various substituted styrenes which is represented by the following formula



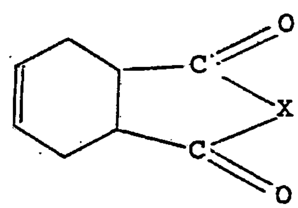
wherein R is hydrogen, an alkyl group containing from 1 to about 6 carbon atoms, or halogen; Z is a member selected from the group consisting of vinyl, halogen and alkyl groups containing from 1 to about 6 carbon atoms; and p is a whole number from 0 up to the number of replaceable hydrogen atoms on the phenyl nucleus. Specific examples of vinyl aromatic compounds such as represented by the above formula include, for example, in addition to styrene, alpha-methyl styrene, beta-methyl styrene, vinyl toluene, 3-methyl styrene, 4-methyl styrene, 4-isopropyl styrene, 2,4-dimethyl styrene, o-chloro styrene, p-chloro styrene, o-bromo styrene, 2-chloro-4-methyl styrene, etc. Styrene is the preferred vinyl aromatic compound.

The maleic anhydride and maleimide derivative compounds utilized in the formation of the copolymers with vinyl aromatic compounds may generally be represented by the formula

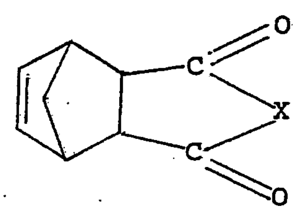


wherein each R group is hydrogen or an aliphatic or aromatic hydrocarbyl group or the two R groups are joined together to form a fused ring derivative, X is -O- or >NR^2 where R_2 is a hydrocarbyl group which may be an aliphatic or an aromatic hydrocarbyl group such as phenyl, methyl, ethyl, propyl, butyl, etc. Preferably both R groups are hydrogen.

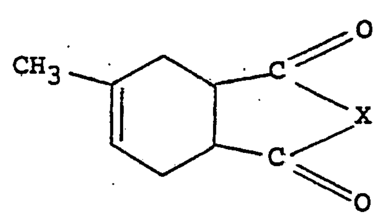
Examples of maleic derivatives which are cyclic or bicyclic compounds include



obtained by a Diels-Alder reaction of butadiene with maleic anhydride or a maleimide



obtained by a Diels-Alder reaction of cyclopentadiene with maleic anhydride or maleimide, and



obtained by a Diels-Alder reaction of isoprene with maleic anhydride or an N-substituted maleimide maleimide. These cyclic or bicyclic derivatives have high glass transition temperatures.

Copolymers comprising a vinyl aromatic compound and metal salts of maleic acid also are useful as the second polymer in the blended polymer compositions of the present invention. The metals present in the metal salt of maleic acid may be Group I metals, Group II metals or transition metals. Alkali metals and transition metals are preferred. Partial esters of the unsaturated anhydrides also can be used. These can be obtained, for example, by reacting or esterifying, maleic acid or maleic anhydride with less than one equivalent of an alcohol such as methanol, ethanol, propanol, etc.

The copolymers of the vinyl aromatic compounds with maleic anhydride, N-substituted maleimides or metal salts of maleic acid are obtained, in one embodiment, by polymerizing equimolar amounts of styrene and the coreactant, with or without one or more interpolymerizable comonomers. In another embodiment, substantially homogeneous copolymers of styrene with maleic anhydride or maleimide or metal salts of maleic acid can be obtained by (1) heating a vinyl aromatic compound to a temperature at which the vinyl aromatic compound with polymerize, (2) stirring the polymerizing vinyl aromatic compound while (3) adding maleic anhydride, maleimide, or the metal salt of maleic acid, or mixtures thereof at a continuous and uniform rate. Generally, the addition of the maleic anhydride, maleimide, or metal salts or esters of maleic acid is made at a rate in moles per unit time that is slower than the rate, in moles per unit time at which the vinyl aromatic compound is poly-

merizing. Procedures for preparing such copolymers are known in the art and have been described in, for example, U.S. Patent 2,971,939.

In one embodiment, the styrene-maleic anhydride copolymers are preferred second polymers in the blended polymer compositions of the present invention. The styrene-maleic anhydride copolymers (SMA) are available commercially from, for example, ARCO under the general trade designation Dylark. Examples include: Dylark DBK-290 reported to comprise about 18% by weight of maleic anhydride and about 82% by weight of styrene; Dylark 332 reported to comprise about 14% by weight of maleic anhydride and 86% by weight of styrene; and Dylark 134 reported to comprise about 17% by weight of maleic anhydride, the balance being styrene.

Other Dylark materials available include transparent grades: Dylark 132 (Vicat 109°C), Dylark 232 (Vicat 123°C), and Dylark 332 (Vicat 130°C). Impact grades include Dylarks 150, 250, 350 and 700 which are believed to be blends and/or grafts of SMA with SBR.

Other examples of impact modified styrenic and alpha-methyl styrene copolymers with maleic anhydride and acrylonitrile include Arvyl 300 MR and 300 CR.

Low molecular weight styrene-maleic anhydride copolymers (Mw as low as 1500) also are useful and these are available commercially such as from Monsanto under the designation "Scripset" and from Atochem under the designation "SMA Resins". Sulfonated styrene-maleic anhydride copolymers (and their metal salts) also are available and useful in this invention. Two such products are available from Atochem:SSMA-1000 which is a sulfonated copolymer of about 50% styrene and 50% maleic anhydride; and SSMA 3000, a sulfonated SMA comprising about 75% styrene and 25% maleic anhydride.

(B-2) Terpolymers of Vinyl Aromatic Compounds, Unsaturated Dicarboxylic Acid Anhydrides, Imides, Metal Salts or Partial Esters of the Dicarboxylic Acids, and Copolymerizable Unsaturated Monomers.

The terpolymers useful in the present invention comprise (1) a vinyl aromatic compound as described above, (2) unsaturated dicarboxylic acid anhydrides, imides, metal salts or partial esters as described above; and (3) copolymerizable monomers. Examples of copolymerizable monomers used to form the above-described terpolymers include acrylic acid alkyl-substituted acrylic acids, acrylic esters and alkyl-substituted acrylic esters containing from 1 to 4 carbon atoms in the ester moiety, acrylonitriles, and mixtures thereof. Acrylates and methacrylates are preferred comonomers. Examples of such comonomers include methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate. Other vinyl monomers can be utilized as the comonomers, and these include vinyl acetate, vinyl methyl ether, vinyl ethyl ether, vinyl chloride, isobutene, etc.

In one embodiment, the terpolymers comprise about 45 to 83% (preferably 50 or 60 to 75%) by weight of the vinyl aromatic monomer, from 15 to 35% (preferably 20-30%) by weight of an unsaturated dicarboxylic acid anhydride and from 2 to about 20% (preferably 4-10%) by weight of a C_{1-3} alkyl methacrylate ester. Terpolymers of this type are available commercially from Monsanto.

(B-3) Blends or Reaction Products of Elastomers and the Copolymer of (B-1) or Terpolymer of (B-2).

The second polymer utilized in the blended compositions of the present invention may comprise a blend or reaction product of an elastomer and the

copolymer of (B-1) or the terpolymer of (B-2) described above. The elastomers utilized in this embodiment may be polybutadienes, isobutylene-isoprene copolymers, styrene butadiene copolymers, butadiene-acrylonitrile copolymers, ethylene-propylene copolymers, polyisoprenes, ethylene-propylene diene monomer terpolymers (EPDM), etc. Particularly preferred elastomers are the so-called "high-cis" diene rubbers which contain at least 90% by weight of cis-1,4-polybutadiene units. The preferred rubbers generally have a Tg of less than -20°C.

The polymer component (B-3) may comprise blends of the elastomers and the copolymers or terpolymers or the elastomer may be grafted into the copolymer or terpolymer. Alternatively, the polymer component (B-3) may comprise a polymer wherein the elastomer is both blended and grafted into the copolymer or terpolymer. A typical method of preparing the elastomer modified graft copolymers is found in U.S. Patent 3,919,354 which is incorporated herein by reference. Elastomer-modified styrenic terpolymers such as the terpolymers (B-2) are described in U.S. Patent 4,341,695 which also is incorporated by reference.

The amount of elastomer incorporated into the blends or grafts of this embodiment may be up to about 50% by weight of elastomer in the total blend or graft. Elastomer-modified graft vinyl aromatic maleic anhydride copolymers are available commercially from ARCO Polymers Inc. (ARCO) under the general designations Dylark and Arvyl. Examples of such elastomer-modified copolymers include Dylark DKB-218 which is reported to comprise about 10% by weight of elastomer in the total graft copolymer, 17% by weight of maleic anhydride and 83% by

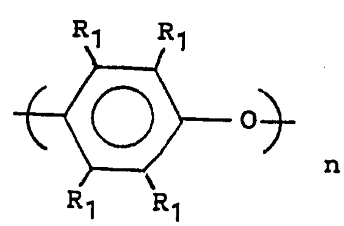
weight of styrene in the resin phase; Dylark 338S reported to comprise 4% by weight of elastomer in the total graft copolymer, and 14% by weight of maleic anhydride and 86% by weight of styrene in the resin phase; Dylark 350 reported to comprise 15% by weight of rubber in the total graft polymer and 13% by weight of maleic anhydride and 87% by weight of styrene in the resin phase.

Blends or reaction products of SMA copolymers and polybutylene terephthalate (PBT) (50:50) are useful, and these are available from Arco under the general designation Dylark DPN-500 series. Blends of SMA with polycarbonates are available under the designation Arloy.

Blends or reaction products of elastomers with terpolymers (B-2) also are available from the Monsanto Chemical Company under the general trade designation "Cadon". Cadon is reported to be a blend of a reaction product of polybutadiene with a styrene:maleic anhydride:methyl methacrylate terpolymer.

(B-4) Blends Comprising a Polymer of a Vinyl Aromatic Compound and a Polyarylene Ether and, Optionally an Elastomer.

Blends comprising a polymer of a vinyl aromatic compound and a polyarylene ether are also useful as the second polymer in the blended polymer compositions of the present invention. Among the preferred polyarylene ethers are polyphenylene ethers which may be represented by the following formula



wherein the oxygen ether atom of one unit is connected to the phenyl nucleus of the next adjoining unit; each R_1 is independently a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon groups free of a tertiary alpha-carbon atom, halohydrocarbon groups having at least 2 carbon atoms between the halogen atom and the phenyl nucleus and also being free of a tertiary alpha-carbon atom, hydrocarbonoxy groups free of aliphatic, tertiary alpha-carbon atoms and halohydrocarbonoxy groups containing at least 2 carbon atoms between the halogen atom and the phenyl nucleus and being free of an aliphatic, tertiary alpha-carbon atom; n is an integer of at least about 50 such as from about 50 to about 800 and preferably from about 100 to about 300. Such polyarylene ethers may have molecular weights in the range of between 1000 and 100,000 and more preferably between about 6000 and 100,000. A preferred example of a polyarylene ether is poly(2,6-dimethyl-1,4-phenylene)ether. Examples of polyphenylene ethers useful in the blended polymer compositions of the present invention and methods for their preparation are described in, for example, U.S. Patents 3,306,874; 3,306,875; 3,257,357; and 3,257,358, and these patents are incorporated by reference for their disclosures of such polymers.

Typical styrene polymers which can be blended or reacted with the polyphenylene ethers include, for example, homopolymers such as polystyrene and polychlorostyrene, modified polystyrenes such as rubber-modified polystyrenes (high impact styrenes) and the styrene-containing copolymers such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-acrylonitrile-alpha-alkyl styrene copolymers, styrene-

acrylonitrile-butadiene copolymers (ABS), poly-alpha-methyl styrene, copolymers of ethyl vinyl benzene and divinyl benzene, etc.

Blends of styrene resins with these polyarylene ethers such as polyphenylene ethers are particularly useful in this invention and are available commercially. For example, blends comprising polystyrene and polyphenylene ether typically containing from about 25 to about 50% by weight of polystyrene units are commercially available from the General Electric Company under the tradename NORYL® thermoplastic resin. The molecular weight of such blends may range from about 10,000 to about 50,000 and more often will be about 30,000.

The elastomers which may be included in the blends of or reacted with the polymer of a vinyl aromatic compound and a polyarylene oxide include the elastomers described above with respect to polymer type (B-3).

(B-5) <u>Copolymers and Terpolymers of a Vinyl Aromatic Compound With an Acrylic Ester and/or Alkyl-Substituted Acrylic Ester</u>.

The second polymer utilized in the blended polymer compositions of the present invention may comprise terpolymers of a vinyl aromatic compound with an acrylic ester and/or an alkyl-substituted acrylic ester. Vinyl aromatic compounds such as those described above and including styrene and substituted styrenes may be utilized in the preparation of these particular copolymers. The acrylic ester and alkyl-substituted acrylic esters useful in preparing these polymers include esters characterized by the following formula

$$CH_2=C(R_1)COOR_2$$

wherein R_1 is hydrogen, a lower alkyl group containing from 1 to 4 carbon atoms, or a halogen; and R_2 is a lower alkyl group containing from 1 to about 4 carbon atoms. Specific examples of esters characterized by the above Formula I include methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, ethyl ethacrylate, etc.

The polymers of a vinyl aromatic compound such as styrene with an acrylic ester and/or an alkyl-substituted acrylic ester can be prepared by procedures well-known to those skilled in the art. The mole ratio of vinyl aromatic compound to acrylic ester and/or alkyl-substituted ester may vary over a wide range such as from about 10:90 to about 90:10. Such terpolymers are available commercially from CYRO under the designations "XT Polymer Series" and "Cyrolite G-Series". These terpolymers are referred to as acrylic-based multipolymer products. They are believed to be terpolymers of styrene, methyl methacrylate and ethyl acrylate. Some of the products may be impact modified with polybutadiene during copolymerization.

Other acrylic based multipolymer products are available from Polysar under the designation "Zylar 90". This product is believed to comprise styrene, butadiene and methyl methacrylate.

(B-6) <u>Product of the Reaction of an Alpha,Beta-Olefinically Unsaturated Carboxylic Reagent and a Hydrogenated Block Copolymer</u>.

Also useful in the blended polymer compositions of the present invention are polymeric products of the reaction of an alpha,beta-olefinically unsaturated carboxylic reagent in a hydrogenated block copolymer of a vinyl aromatic compound and an aliphatic conjugated

diene. The hydrogenated block copolymers of a vinyl aromatic compound and an aliphatic conjugated diene may be either normal block copolymers (true block copolymers) or random block copolymers, although the normal block copolymers are preferred. The vinyl-substituted aromatic compounds generally contain from about 8 to about 12 carbon atoms and preferably about 8 or 9 carbon atoms. Examples of such vinyl aromatic compounds include styrene and the various substituted styrenes described above. The conjugated dienes used to form the block copolymers generally contain from about 4 to about 10 carbon atoms, and preferably from 4 to about 6 carbon atoms. Examples of such conjugated dienes include a 2,3-dimethyl-1,3-butadiene, chloroprene, isoprene, and 1,3-butadiene. Isoprene and 1,3-butadiene are particularly preferred, and mixtures of such conjugated dienes may be used.

The normal block copolymers have a total of from 2 to about 5, and preferably 2 or 3 polymer blocks of the vinyl-substituted aromatic and the conjugated diene, with at least one polymer block of said vinyl-substituted aromatic and at least one polymer block of said conjugated diene being present. The vinyl substituted aromatic content of these copolymers is in the range of from about 20% to about 70% by weight and preferably from about 40% to about 60% by weight. The block copolymers can be prepared by conventional methods well-known to those in the art, and these copolymers usually are prepared by anionic polymerization using, for example, an alkali metal hydrocarbon such as sec-butylithium as a polymerization catalyst.

The block copolymers of the vinyl aromatic compound and a conjugated diene are hydrogenated prior

to reaction with the olefinically unsaturated carboxylic acid to remove virtually all of the olefinic double bonds. Techniques for accomplishing this hydrogenation are well-known to those skilled in the art. Generally, hydrogenation is accomplished by contacting the copolymers with hydrogen at superatmospheric pressure in the presence of a metal catalyst such as colloidal nickel, palladium supported on charcoal, etc. These block copolymers typically have number average molecular weights in the range of about 10,000 to about 500,000, and preferably from about 30,000 to about 200,000.

The alpha,beta-olefinically unsaturated carboxylic reagent includes the carboxylic acids per se and functional derivatives thereof such as anhydrides, esters, amides, imides, salts, acyl halides, etc. The carboxylic acid reagents may be either monobasic or polybasic in nature, and when polybasic, they are preferably dicarboxylic acids. The monobasic alpha,beta-olefinic unsaturated carboxylic acid reagents are carboxylic acids corresponding to the formula

$$RCH{=}C(R_1)COOH$$

wherein R is hydrogen or a saturated aliphatic or alicyclic, aryl, alkaryl or heterocyclic group. Preferably, R is hydrogen or an alkyl group containing from 1 to about 10 carbon atoms; R_1 is hydrogen or an alkyl group containing from about 1 to about 10 carbon atoms. The total number of carbon atoms in R and R_1 should not exceed 18 carbon atoms. Specific examples of useful monobasic alpha,beta-olefinic unsaturated carboxylic acids include acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, etc.

As noted above, the olefinic unsaturated carboxylic acid reagent may be a dibasic acid. Examples of useful dibasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid. A preferred alpha,beta-olefinically unsaturated carboxylic acid reagent is maleic anhydride.

The amount of alpha,beta-olefinically unsaturated carboxylic reagent reacted with the block copolymers is an amount which is effective to modify the properties of the block copolymers in a desired manner. Generally, the amount of reagent will be from about 0.2 to about 20% by weight and preferably from about 0.5 to about 5% by weight based on the total weight of the block copolymer and the reagent.

In order to promote the reaction to generate reaction cites, free radical initiators are utilized, and these initiators usually are either peroxides or various organic azo compounds. The amount of initiator utilized generally is from about 0.01% to about 5% by weight based on the combined weight of the block copolymer in the carboxylic reagent. The amount of carboxylic reagent incorporated into the block copolymers can be measured by determining the total acid number of the product.

(B-7) Polycarbonates.

The polycarbonates utilized in the preparation of the blends of this invention may be characterized by the formulae

$$\left(-Ar-A-Ar-O-C(O)O- \right)_n$$

and

$$-\!\!\left(\!-Ar-O-C(O)O-\!\right)\!\!-_n$$

wherein Ar is selected from the group consisting of phenylene and alkyl, alkoxyl, halogen and nitro-substituted phenylene; A is selected from the group consisting of carbon-to-carbon bonds, alkylidene, cycloalkylidene, alkylene, cycloalkylene, azo, imino, sulfur, oxygen, sulfoxide and sulfone, and n is at least 2.

The preparation of the polycarbonates is well-known and the details thereof need not be delineated herein. There are a variety of preparative procedures set forth in <u>Chemistry and Physics of Polycarbonates</u> by Herman Schnell, Interscience Division of John Wiley & Company, New York, (1964), first edition, as well as in U.S. Patent 3,028,365. In general, a preferred reaction is carried out by dissolving a dihydroxy component in a base such as pyridine and bubbling phosgene into the stirred solution at the desired rate. Tertiary amines may be used to catalyze the reaction as well as to act as acid acceptors throughout the reaction. Since the reaction is normally exothermic, the rate of phosgene addition can be used to control the reaction temperature. The reactions generally utilize equimolar amounts of phosgene and dihydroxy reactants, however, the molar ratios can be varied dependent upon the reaction conditions.

A preferred polycarbonate utilized in this invention is obtained when Ar is p-phenylene and A is isopropylidene. This polycarbonate is prepared by reacting para, para'-isopropyldienediphenol with phosgene and is sold by General Electric Company under the trademark LEXAN® and by Mobay under the trademark MERLON®. This commercial polycarbonate typically has a

molecular weight of around 18,000, and a melt temperature of over 230°C. Other polycarbonates may be prepared by reacting other dihydroxy compounds, or mixtures of dihydroxy compounds, with phosgene. The dihydroxy compounds may include aliphatic dihydroxy compounds although for best high temperature properties aromatic rings are essential. The dihydroxy compounds may include within the structure diurethane linkages. Also, part of the structure may be replaced by siloxane linkage. These and other variations of polycarbonate structure are described in the Schnell reference cited above. The same reference presents a long list of monomers (particularly dihydroxy compounds) that may be used in polycarbonate synthesis.

(B-8) Graft Copolymer of a Monoethylenically Unsaturated Resin Forming Monomer and EPDM Type Elastomers.

The blended polymer compositions of the present invention may contain a graft copolymer of a monoethylenically unsaturated resin forming monomer on an EPDM type of rubber. The monoethylenically unsaturated resin-forming monomers include monomers such as styrene, halo styrene, alpha-methyl styrene, para-methyl styrene, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, maleic anhydride, the lower (1-8 carbon atoms), alkyl esters of acrylic acid and methacrylic acid, etc. Monomers of particular interest are styrene, methyl methacrylate, mixtures of styrene and acrylonitrile, mixtures of styrene and methyl methacrylate, etc.

The terpolymers or rubbery polymers comprise two different linear alpha-monoolefins and a non-conjugated diene. One of the alpha-olefins is ethylene and the other is a higher alpha-monoolefin containing 3 to 16 carbon atoms such as propylene, 1-butene, 1-octene,

etc. Examples of useful non-conjugated dienes include the 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene, etc. The weight ratio of the ethylene to the higher alpha-monoolefin in the terpolymer is ordinarily within the range of from 20:80 to 80:20. The amount of diene should be such that the iodine number of the terpolymer is in the range of from about 15 to about 40, preferably from about 20 to about 35 which corresponds generally to about 7 to 20 weight percent and preferably from 9 to 17 weight percent of the diene monomer units in the terpolymer.

The weight ratio of the monoethylenically unsaturated resin-forming monomer to the terpolymer is from about 95:5 to 30:7. In one embodiment, the resin forming monomer is polymerized in situ in the presence of the terpolymer. The specific example of a graft copolymer is a graft copolymer of styrene and acrylonitrile on ethylene-propylene-5-ethylidene-2-norbornene terpolymer wherein the terpolymer comprises 60 weight percent ethylene, 30 weight percent propylene and 10% of the norbornene monomer. Graft copolymers of the type useful in the present invention, and methods of preparing such graft copolymers are described in, for example, U.S. Patents 4,202,948 and 4,166,081 which are hereby incorporated by reference. Graft copolymers are commercially available such as from Dow Chemical Company under the trade designation "Rovel".

(B-9) <u>Acrylic Polymers</u>.

The blended polymer compositions of the present invention may contain acrylic polymers including acrylic polymers derived from acrylic esters and methacrylic esters. Generally acrylic polymers are based on methyl methacrylate monomer (MMA). The acrylic monomers may be

polymerized by free radical processes using peroxides. MMA may be homopolymerized or copolymerized with other acrylates such as methyl or ethyl acrylate. Acrylic polymers which have been modified with various ingredients also can be utilized, and these various ingredients include butadiene, styrene, vinyl and butyl acrylate which increase impact strength of the acrylics.

(B-10) Nitrile Resins.

Nitrile resins also may be used as the second polymer in the blended compositions of the present invention. Nitrile resins or polymers based upon acrylonitrile, and the polymers have moderately high tensile properties, good impact properties when modified with rubber or oriented, good gas barrier properties, good chemical resistance and good taste and odor-retention properties.

The nitrile resins (B-10) are preferably those thermoplastic materials having an alpha,beta-olefinically unsaturated mononitrile content of 50% by weight or greater. These nitrile barrier resins may be copolymers, grafts of copolymers onto a rubbery substrate, or blends of homopolymers and/or copolymers.

The alpha,beta-olefinically unsaturated mononitriles encompassed herein have the structure

$$CH_2=C(R)CN$$

where R is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen. Such compounds include acrylonitrile, alpha-bromoacrylonitrite, alpha-fluoroacrylonitrile, alpha-methacrylonitrile, alpha-ethacrylonitrile, and the like. The most preferred olefinically unsaturated nitriles in the present invention are acrylonitrile, methacrylonitrile and mixtures thereof.

These nitrile resins may be divided into several classes on the basis of complexity. The simplest molecular structure is a random copolymer, predominantly acrylonitrile or methacrylonitrile. The most common example is a styrene-acrylonitrile copolymer. Block copolymers of acrylonitrile, in which long segments of polyacrylonitrile alternate with segments of polystyrene, or of polymethyl methacrylate, are also known.

Simultaneous polymerization of more than two comonomers produces an interpolymer, or in the case of three components, a terpolymer. A large number of comonomers for the acrylonitrile are possible. These include lower alpha olefins of from 2 to 8 carbon atoms, e.g., ethylene, propylene, isobutylene, butene-1, pentene-1, and their halogen and aliphatic-substituted derivatives as represented by vinyl chloride, vinylidene chloride, etc.; monovinylidene aromatic hydrocarbon monomers of the general formula

$$Ar{-}C(R_1){=}CH_2$$

wherein R_1 is hydrogen, chlorine or methyl and Ar is an aromatic group of 6 to 10 carbon atoms which may also contain substituents such as halogen and alkyl groups attached to the aromatic nucleus, e.g., styrene, alpha methyl styrene, vinyl toluene, alpha chlorostyrene, ortho chlorostyrene, para chlorostyrene, meta chlorostyrene, ortho methyl styrene, para methyl styrene, ethyl styrene, isopropyl styrene, dichloro styrene, vinylnaphthalene, etc. Especially preferred comonomers are isobutylene and styrene.

Another group of comonomers are vinyl ester monomers of the general formula

$$R_3C(H)=C(H)-OC(O)R_3$$

wherein each R_3 is independently selected from the group comprising hydrogen, alkyl groups of from 1 to 10 carbon atoms, aryl groups of from 6 to 10 carbon atoms including the carbon atoms in ring-substituted alkyl substituents; e.g., vinyl formate, vinyl acetate, vinyl propionate, vinyl benzoate and the like.

Similar to the foregoing and also useful are the vinyl ether monomers of the general formula

$$H_2C=C(H)-OR_4$$

wherein R_4 is an alkyl group of from 1 to 8 carbon atoms, an aryl group of from 6 to 10 carbon atoms, or a monovalent aliphatic radical of from 2 to 10 carbon atoms, which aliphatic radical may be hydrocarbon or oxygen-containing, e.g., an aliphatic radical with ether linkages, and may also contain other substituents such as halogen, carbonyl, etc. Examples of these monomeric vinyl ethers include vinyl methyl ether, vinyl ether ether, vinyl n-butyl ether, vinyl 2-chloroethyl ether, vinyl phenyl ether, vinyl isobutyl ether, vinyl cyclohexyl ether, 4-butyl cyclohexyl vinyl ether or p-chlorophenyl glycol, etc.

Other comonomers are those comonomers which contain a mono- or dinitrile function. Examples of these include methylene glutaronitrile, (2,4-dicyanobutene-1), vinylidene cyanide, crotonitrile, fumarodinitrile, maleodinitrile.

Other comonomers include the esters of olefinically unsaturated carboxylic acids, preferably the lower alkyl esters of alpha,beta-olefinically unsatur-

ated carboxylic acids and more preferred the esters having the structure

$$CH_2{=}C(R_1)COOR_2$$

wherein R_1 is hydrogen, a halogen, or an alkyl group having 1 or 2 carbon atoms and R_2 is hydrogen or an alkyl group having from 1 to 8 carbon atoms. Compounds of this type include methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, methyl alpha-chloroacrylate, and the like. Most preferred are methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl acrylate and butyl methacrylate.

Another class of nitrile resins are the graft copolymers which have a polymeric backbone on which branches of another polymer chain are attached or grafted. Generally the backbone is preformed in a separate reaction. Polyacrylonitrile may be grafted with chains of styrene, vinyl acetate, or methyl methacrylate, for example. The backbone may consist of one, two, three, or more components, and the grafted branches may be composed of one, two, three or more comonomers.

The methods of forming these various nitrile resins and examples of these resins can be found in the following U.S. Patents 3,325,458; 3,336,276; 3,426,102; 3,451,538; 3,540,577; 3,580,974; 3,586,737; 3,634,547; 3,652,731; and 3,671,607.

The chemical composition of the nitrile resins in general useful as resin (B-10) may be varied considerably, but in general, useful nitrile resins will include about 70% by weight of acrylonitrile monomer, 20 to 30% methyl acrylate or styrene as a comonomer and from 0 to about 10% butadiene as the impact-modifying

termpolymer. Nitrile polymers of these types are offered commercially under the trade designation Barex resins supplied by BP Chemicals International.

(B-11) Acrylic-Styrene-Acrylonitrile Polymers.

The blended polymer compositions of the present invention may contain one or more acrylic-styrene-acrylonitrile polymers. These terpolymers are often referred to as "ASA". The ASA polymers are generally similar to ABS resins with regard to properties. The type and amount of the monomers used to prepare these terpolymers may be varied, and the choice will be dependent in part on the properties desired. Various acrylic monomers, styrene monomers and acrylonitrile monomers can be used in various combinations. For example, alpha-methylstyrene or methacrylonitrile also can be used. An example of a commercially available acrylic-styrene-acrylonitrile terpolymer is the polymer available from General Electric Company under the designation Geloy. Other examples include an acrylic:styrene:methacrylonitrile terpolymer.

(B-12) Acrylonitrile-Halogenated Polyolefin-Styrene Terpolymers.

The blended polymer compositions of the invention also may include at least one acrylonitrile-halogenated polyolefin-styrene terpolymer. These terpolymers often are referred to as ACS polymers when the halogen is chlorine. A commercially available example of such terpolymers is an acrylonitrile-chlorinated polyethylene-styrene terpolymer which is available in three grades: flame retardant, weather resistant, and optical reflector. These terpolymers are manufactured by the Specialty Plastics Division of Showa Denko K.K.

(C) Compatibilizing Agent.

The polymer blends of the present invention also contain at least one compatibilizing agent which may be block copolymers selected from the group consisting of diblock, triblock, multiblock, starblock, polyblock or graftblock copolymers of a vinyl aromatic compound and a conjugated diene, or their partially hydrogenated derivatives and mixtures thereof. The choice of compatibilizing agent included in the blended polymer compositions of the invention may depend upon the type of polymers (A) and (B) included in the blend.

In one preferred embodiment, the compatibilizing agent is at least one multiblock, starblock, polyblock or graftblock copolymer with multiblock copolymers being particularly preferred. In another preferred embodiment, the compatibilizing agent is a multiblock copolymer as described above comprising at least about 40% by weight of styrene, and more often, from about 40 to about 75% by weight of styrene. Many of the characteristics of the block copolymers can be varied and controlled by balancing between the hard (polystyrene) and rubber (polydiene) components, and utilizing linear or branched structures with different molecular weights.

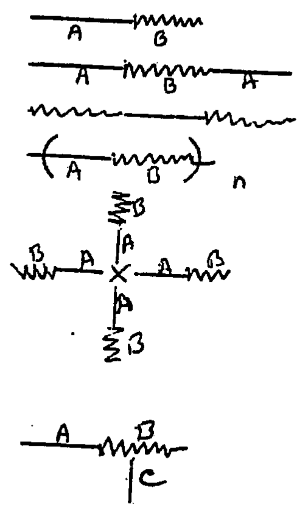
Throughout this specification and claims, the terms diblock, triblock, multiblock, polyblock, and graft or grafted-block with respect to the structural features of block copolymers are to be given their normal meaning as defined in the literature such as in the Encyclopedia of Polymer Science and Engineering, Vol. 2, (1985) John Wiley & Sons, Inc., New York, pp. 325-326, and by J.E. McGrath in Block Copolymers, Science Technology, Dale J. Meier, Ed., Harwood Academic Publishers, 1979, at pages 1-5. In particular, the

structure of the various block copolymers may be illustrated as follows:

TABLE 1

Block Copolymers[1]

diblock copolymer	A-B or
triblock copolymer	A-B-A
	B-A-B
multiblock copolymer[2]	$(A-B)_n$
starblock copolymer[3]	B A B-A-X-A-B A B
graft- or grafted-block copolymer	A-B C



[1] —— hard —ʌʌʌ— soft.

[2] Sometimes designated segmented or poly block copolymers, n is >1.

[3] X is a junction unit, also called radial block.

It will be understood that blocks A and B and C may be either homopolymer or random copolymer blocks as long as each block predominates in at least one class of the monomers characterizing the blocks and as long as the A block is predominantly a vinyl aromatic compound and the B block is predominantly a diene or its hydrogenated derivatives. The vinyl aromatic compounds which may be present in the block copolymers utilized in the present invention may be any of the vinyl aromtic compounds described above with respect to polymer component (B-1) and (B-2). Preferred vinyl aromatic

compounds are styrene and alpha-methyl styrene with styrene being particularly preferred. The conjugated dienes may contain from 4 to 10 carbon atoms and more generally contain from about 4 to about 6 carbon atoms. Butadiene and isoprene are particularly preferred conjugated dienes useful in preparing the block copolymer compatibilizers useful in the present invention.

Partially hydrogenated block copolymer derivatives also are useful as compatibilizers in the polymer compositions of the present invention. The conjugated diene portion of the block copolymer is at least 90% saturated and more often at least 95% saturated while the vinyl aromatic portion is not significantly hydrogenated. More particularly useful hydrogenated block copolymer is the block copolymer of polystyrene-polyisoprene-polystyrene which has been hydrogenated to a polystyrene-poly(ethylene/propylene)-polystyrene block polymer. When a polystyrene-polybutadiene-polystyrene block copolymer is hydrogenated, it is desirable that the 1,2-polybutadiene to 1,4-polybutadiene ratio in the polymer is from about 30:70 to about 70:30. When such a block copolymer is hydrogenated, the resulting product resembles a regular copolymer block of ethylene and butene-1 (EB). As noted above, when the conjugated diene employed as isoprene, the resulting hydrogenated product resembles a regular copolymer block of ethylene and propylene (EP).

Hydrogenation of the precursor block copolymers can be effected by known techniques such as by the use of a catalyst comprising the reaction product of an aluminum alkyl compound with nickel or cobalt carboxylates or alkoxides under conditions which result in substantial complete hydrogenation of at least 80% of

the aliphatic double bonds while hydrogenating 25% of the vinyl aromatic double bonds remaining in the polymer. Preferred hydrogenated copolymers of those wherein at least 99% of the aliphatic double bonds are hydrogenated while less than 5% of the aromatic double bonds are hydrogenated.

The average molecular weights of the individual blocks within the copolymers may vary within certain limits. In most instances, the vinyl aromatic block will have a number average molecular weight in the order of about 5000 to about 125,000, and preferably between about 7000 and 60,000. The conjugated diene blocks either before or after hydrogenation will have number average molecular weights in the order of about 10,000 to about 300,000 and more preferably from about 30,000 to 150,000. The total number average molecular weight of the block copolymers is typically in the order of about 25,000 to about 250,000.

Specific examples of diblock copolymers include styrene-butadiene, styrene-isoprene, and the hydrogenated derivatives thereof. Examples of triblock polymers include styrene-butadiene-styrene, styrene-isoprene-styrene alpha-methylstyrene-butadiene-alpha-methylstyrene, alpha-methylstyrene-isoprene-alpha-methylstyrene, and their partially hydrogenated derivatives. The diblock and triblock polymers are commercially available from a variety of sources under various tradenames. Examples of commercially available diblock resins include Solprene 314D (Phillips) and K Resin 04 (Phillips). A number of styrene-butadiene-styrene triblock copolymers are sold by the Shell Chemical Company under the trademarks "Kraton 2103", "Kraton 2104", and "Kraton 2113". Such thermoplastic rubbery block copolymers are made by

anionic polymerization, and the above three identified Shell Kratons differ in molecular weight and viscosity, and also in the ratio of butadiene to styrene. For example, "Kraton 2103" and "Kraton 2113" have a styrene to butadiene ratio of 28:72 while "Kraton 2104" as a styrene to butadiene ratio of 30:70. Blends of diblock and triblock copolymers are also available. Kraton 1118 (Shell) is a blend of SB diblock and SBS triblock copolymers. A Kraton G-1652 is a hydrogenated SBS triblock comprising 30% styrene end blocks and a midblock equivalent to a random copolymer of ethylene and 1-butene (EB). This copolymer is sometimes designated as SEBS.

Functionalized block copolymers such as those obtained by reacting a block copolymer with maleic anhydride also are useful in this invention. Kraton FG 1901X is a maleated SEBS block copolymer available from Shell.

Multiblock copolymers of styrene and either isoprene or butadiene also are commercially available. Commercially available and preferred styrene-butadiene multiblock copolymers include Stereon 840A, Stereon 841A and Stereon 845A which are available from The Firestone Tire & Rubber Company.

Starblock copolymers of styrene and isoprene or styrene and butadiene are commercially available from Phillips Petroleum Company under such designations as "K-Resin". Generally, the K-Resins have a high polystyrene content such as about 75%, and these resins are transparent and rigid. One particularly preferred starblock copolymer is K-Resin KR03 from Phillips. A similar material (75% styrene:25% butadiene) is available from Fina under the designation "Finaprene 520". Radial or starblock copolymers also are available from

Fina under the general designation "Finaprene SBS Polymer". Various grades are available containing from 20% to 40% of styrene.

The relative amounts of the two or more polymers and compatibilizers utilized in the blended polymer compositions of the present invention may vary over a relatively wide range depending on the specific materials used, the desired properties, and particular end use for the blended polymer compositions of the invention. Thus, the blended polymer compositions of the present invention may comprise

(A) from 1 to about 99% by weight of at least one olefin polymer;

(B) from 1 to about 99% by weight of at least one styrenic polymer or any of the polymers and polymer blends identified herein as components (B-1) through (B-12); and

(C) from 1 to about 40% by weight and more generally from 1 to about 15% of the compatibilizer.

In one embodiment of the invention, the compositions of the present invention comprise from about 49 to about 90% by weight of polyolefin (A), 10 to about 30% of the polymer or polymer blend (B-1) through (B-12), and from about 2 to about 10% by weight of the compatibilizing agent.

Generally, the order of mixing of the polymers (A) and (B) and the compatibilizers (C) is not critical. Accordingly, it is possible to mix the compatibilizer with the polyolefin and other polymers by mixing all of the components at the same time. Alternatively, the order of mixing can be varied in order to match the relative viscosities of the various components. The blended polymer compositions of the present invention

may be true blends of the polymers and compatibilizers, or some grafting of the compatibilizers to either or both of the polymers or another compatibilizer are possible.

The blended polymer compositions of the present invention may contain, in addition to the components identified above as components (A), (B) and (C) other components added to modify the properties of the blended polymer composition. The blended polymer compositions of the invention may be compounded further with other polymers (e.g., barrier resins), oils, fillers, coupling agents, reinforcements, antioxidants, stabilizers, fire-retardants, foaming agents, colorants, processing aids, etc. Such additives are selected to provide or modify desirable characteristics of the products prepared from the compositions.

(D) Barrier Resins.

The blended polymer compositions of the present invention may contain at least one resin referred to in the art as a barrier resin. Barrier resins are characterized as having low gas and vapor transmission properties. Any of the known barrier resins may be utilized as component (D) in the blended polymer compositions of the present invention. Particular examples of useful barrier resins (D) include resins selected from the group consisting of vinylidene chloride polymers, and copolymers of vinylidene chloride with one or more mono-ethylenically unsaturated monomers which are copolymerizable with the vinylidene chloride; copolymers of ethylene and vinyl alcohol (EVOH), polyamides, and nitrile resins comprising alpha,beta-olefinically unsaturated aliphatic mono-nitrile polymers and copolymers. When utilized in the blended polymer compositions of the

invention, the barrier resin (D) generally is present in amounts of from 0.1 to about 20% by weight based on the total weight of polymer and resin. It should be noted that polymer (B-10) has previously been described as a nitrile resin. Thus, when the blended polymer compositions include a nitrile resin (B-10) as the second polymer (B), it is generally not necessary to add additional nitrile resin as a barrier component, and it may not be necessary to add any additional barrier resin to the blended polymer composition.

Vinylidene chloride polymers and copolymers are useful barrier materials. Copolymers are particularly useful and these include copolymers having polymerized therein vinylidene chloride in an amount of from about 40 to about 98% by weight and at least one monoethylenically unsaturated monomer which is copolymerizable with the vinylidene chloride in an amount of from about 60% to about 2% by weight. The copolymerizable monomer may be a vinyl functional monomer such as vinyl chloride; alkyl esters of acrylic and methacrylic acids such as alkyl acrylates and alkyl methacrylates; ethylenically unsaturated mono- and dicarboxylic acids such as acrylic acid, methacrylic acid, and itaconic acids; and cyano-functional monomers such as acrylonitrile and methacrylonitrile.

Ethylene vinyl alcohol copolymers (EVOH) that are useful as barrier resins in the compositions of the present invention generally will contain at least about 55% and as much as 80% by weight of vinyl alcohol, and the remainder of the molecule consists essentially of ethylene. These copolymers generally are prepared by hydrolysis of ethylene vinyl acetate copolymers, and, therefore, some vinyl acetate may remain in the resin.

The EVOH copolymers typically have molecular weights in the range of from about 20,000 to 30,000. The EVOH copolymers useful as barrier resins in the compositions of the present invention are commercially available such as from the EVAL Company of America.

Polyamides may also be incorporated into the blended polymer compositions of the present invention to serve as barrier compositions. The polyamides are condensation products which contain recurring aromatic and/or aliphatic amide groups in integral parts of the main polymer chain. Such polyamide products are known generically as "nylons". These polyamides may be prepared by polymerizing a monoamino carboxylic acid or an internal lactam thereof having at least 2 carbon atoms between the amino and the carboxylic acid groups. Alternatively, the polyamides may be obtained by a polymerizing dicarboxylic acid with a diamine which contains at least 2 carbon atoms between the amino groups. Another procedure for preparing polyamides is to polymerize a monoamino carboxylic acid or an internal lactam thereof with a substantially equimolar portion of a diamine and a dicarboxylic acid. Examples of amino carboxylic acids and lactams include epsilon-amino caproic acid, butyrolactam, pivalolactam, caprolactam, capryllactam, undecanolactam and 3- and 4-aminobenzoic acids. Examples of diamines include diamines containing up to 16 carbon atoms such as trimethylenediamine, tetramethylenediamine, pentamethylenediamine, octamethylenediamine, decamethylenediamine, hexadecamethylenediamine and in particular, hexamethylenediamine. Aromatic amines such as p-phenylenediamine, 4,4'-diaminodiphenylsulfone, etc., may be utilized.

The dicarboxylic acids used to form the nylons may be aromatic, for example, isophthalic or terephthalic acids or aliphatic dicarboxylic acids represented by the formula HOOCYCOOH wherein Y represents a divalent aliphatic group containing at least 2 carbon atoms. Examples of such aliphatic dicarboxylic acids include sebacic acid, octadecanoic acid, suberic acid, azelaic undecanedioic acid, glutaric acid, pimelic acid, and especially adipic acid. Specific examples of polyamides useful as barrier compounds in the present invention include:

polyhexamethylene adipamide (nylon 6:6),
polypyrrolidone (nylon 4),
polycaprolactam (nylon 6),
polyheptolactam (nylon 7),
polycapryllactam (nylon 8), etc.

The number average molecular weights of the polyamides used in the polymer blends of the present invention are generally above about 10,000.

The nitrile barrier resins may be any of the resins identified earlier as polymer (B-10).

Commercial examples of nitrile barrier resins include BAREX® 210 resin by BP Chemicals International, an acrylonitrile-based high nitrile resin containing over 65% nitrile, and Monsanto's LOPAC® resin containing over 70% nitrile, three-fourths of it derived from methacrylonitrile.

(E) Fillers and Fibers.

The blended polymer compositions of the present invention may contain one or more fillers of the type used in the polymer art. Examples of fillers employed in a typical compounded polymer blend according to the present invention include talc, calcium carbonate, mica,

wollastonite, dolomite, glass fibers, boron fibers, carbon fibers, carbon blacks, pigments such as titanium dioxide, or mixtures thereof. Preferred fillers are a commercially available talc such as R.T. Vanderbilt's Select-O-Sorb and glass fibers. The amount of filler and fibers included in the blended polymers may vary from about 1% to about 70% of the combined weight of polymer and resin. Generally amounts of 5% to 30% are included.

The fillers and fibers may be treated with coupling agents to improve the bond between the fillers and fibers to the resin. For example, the fillers can be treated with materials such as fatty acids (e.g., stearic acid), silanes, maleated polypropylene, etc. The amount of coupling agent used is an amount effective to improve the bond between the fillers and fibers with the resin.

The blended polymer compositions of the present invention comprising the olefin polymer, the second polymers as described herein as components (B-1) through (B-12), the compatibilizer (C) and other resins such as barrier resins and additives can be prepared by techniques well known to those skilled in the art. For example, a particularly useful procedure is to intimately mix the polymers using conventional mixing equipment such as a mill, a Banbury, a Brabender, a single or twin screw extruder, continuous mixers, kneaders, etc. For example, the polymers may be intimately mixed in the form of granules and/or powder in a high shear mixer. One preferred process for preparing the blended polymers utilizes the Farrell Continuous Mixer (FCM), CP-23. Short residence times and high shear are readily obtained in a CP-23. "Intimate" mixing means that the

mixture is prepared with sufficient mechanical shear and thermal energy to produce a dispersed phase which is finely divided and homogeneously dispersed in the continuous or principal phase.

Improved mixing is often obtained when the viscosities of the olefin polymer (A) and polymer (B) are similar at the temperature and shear stress of the mixing process. The chance for formation of cocontinuous interlocking networks on cooling is increased when approximately equal molar ratios of polymers (A) and (B) are utilized; for example a 50:50 molar ratio of styrene maleic anhydride copolymer and polyolefin.

The polymer blends of the present invention are characterized as having excellent heat distortion properties as well as excellent strength, toughness, stiffness, gloss, ease of processing and fabrication, improved filler interaction, and shrinkage characteristics, hardness, adherability, moldability, formability, and they are retortable and microwaveable. Another advantage of the blended polymer compositions of the present invention is that they can be recycled in conventional procedures whereby the scrap is comminuted and dry-blended or extrusion-blended with fresh blended polymer, and the polymer blended with scrap does not lose its desirable properties. Accordingly, in one embodiment, the blend of fresh or virgin blended polymers of the invention and scrap polymer is extruded into a sheet which can be used in a multilayer structure, preferably as an inner layer, with sheets of virgin blended polymers of the invention, and/or other layers of, e.g., barrier materials, polyolefins, aliphatic or aromatic polyolefins, etc. The blends of fresh and scrap polymer blends of the invention also can be coextruded into

multilayer structures with any of the other polymer materials discussed above.

In some instances, the low temperature impact strength of materials prepared from the blended polymer compositions of the present invention is improved when compared to the typical performance of olefin polymers such as polyethylene and polypropylene, and, therefore, the blended polymer compositions of the present invention possess the required low temperature impact performance and other physical characteristics required for many applications for which polyolefins cannot be used. The polymer blends of the present invention also exhibit excellent food, oil and fat-resistance and are therefore particularly suited for packaging food products. The polymer blends of the invention can be formed into packages, containers, cups, and other products.

It also has been observed that the blended polymer compositions of the present invention can be processed into shaped articles by extrusion, coextrusion, thermoforming, blow molding, injection molding, compression molding, calendering, laminating, stamping, pultrusion, foaming or die coating of continuous fibers. In particular, shaped articles can be prepared by thermoforming sheets of the blended polymer compositions of the present invention. Sheets of the blended polymer compositions of the present invention can be prepared on an extruder such as a 3.5-inch HPM extruder with a two-stage screw of 30:1 L/D ratio and at a melt temperature of about 445°F (230°C). The extrudate is subsequently passed through polished rolls with a center roll heated to an elevated temperature to form a sheet which exhibits low sag since the polymers are appropriately compatibilized. The blended polymer compositions of the

invention also can be used to form an extrusion coating on long fiber reinforcements such as used in long fiber reinforced thermoplastics.

Scrap material produced from processing of the blended polymer compositions of the present invention such as scrap material produced from thermoforming the multilayer structures of the present invention, may be recovered, reground and recycled for use as a component in the polyolefin-containing layer of the multilayer structures. Such scrap material may contain components from the various layers including the polyolefin-containing layer and barrier layer when present. The amount of scrap utilized in the polyolefin-containing layer may vary widely, and may comprise from 1 to about 99% by weight, and more preferably from about 10 to about 60% by weight of the polyolefin-containing layer.

In one embodiment of the present invention, thermoformable multilayer structures can be prepared which comprise

(I) at least one layer of a blended polymer composition according to the present invention; and

(II) at least one layer of an olefin polymer composition which may comprise any of the olefin polymers and olefin copolymers mentioned previously. In a preferred embodiment, the layer of olefin polymer composition is a layer of filled or unfilled polyethylene or polypropylene.

In another embodiment, the multilayer structure may comprise

(III) at least one layer of a barrier resin such as the high nitrile barrier resins described above. Thus, in one embodiment, a thermoformable multilayer structure may comprise a layer of the polymer blend

composition of this invention and a cap layer on one side of an olefin polymer such as polyethylene or polypropylene or a cap layer of a barrier material (D) as described above, or a cap layer of an aliphatic or aromatic vinyl resin such as polystyrene or polymers and copolymers of acrylic esters and acrylonitrile. In another embodiment a multilayer structure comprises a central layer of the polymer blend composition of the present invention, a cap layer on one side comprising an olefin polymer such as polyethylene or polypropylene and a cap layer on the other side of a barrier material, or vinyl polymer.

The cap layers such as the layers of barrier resin, vinyl polymers, etc., can be applied by coextrusion, laminating, etc., or the second layer can be applied from a solution or a dispersion of the barrier resin or vinyl polymer in water or an organic liquid such as acetone. On drying, a film or cap layer is left on the layer comprising the composition of the invention.

Molded articles having desired shapes can be produced from each of the blended polymer compositions of the present invention by

(A) feeding a sheet of the blended polymer composition of the invention to a heating station;

(B) heating the sheet to its softening point; and

(C) feeding the softened sheet to a forming station where it is molded into articles of the desired shape.

In another embodiment, coextruded multilayered structures can be prepared wherein at least one layer comprises the blended polymer compositions of the pre-

sent invention. In other embodiments, at least one additional layer comprises a polyolefin such as polyethylene or propylene.

Various features and aspects of the present invention are illustrated further in the examples that follow. While these examples are presented to show one skilled in the art how to operate within the scope of this invention, they are not to serve as a limitation on the scope of the invention where such scope is only defined in the claims. Moreover, in the following examples, preparation of blends, compounds, injection molded specimens, mono layer or laminated sheets are illustrated. These examples serve merely as illustrative embodiments of the present invention and are not to be considered limiting.

Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, temperatures are in degrees centigrade and pressures are at or near atmospheric. The physical properties described in the following examples are measured in accordance with ASTM Standard Test Procedures as identified in the following Table 3.

TABLE 3

Property	ASTM Method
Melt Flow Rate	D-1238*
Tensile Strength	D-638
Elongation	D-638
Flexural Strength	D-790
Flexural Modulus (tangent)	D-790
Izod Impact (notched)	D-256**
Izod Impact (unnotched)	D-256
Gardner Impact	D-3209
Heat Deflection Temperature	D-648
Instrumented Impact	D-3763

* Condition 230°C/2.16 kg.
** Method A.

Example 1

The compatible blend of polypropylene (PP), a styrene maleic anhydride copolymer (SMA) and a multi-block styrene-butadiene copolymer (SBR) is prepared on a laboratory Banbury mixer (Farrel) at about 155°C, ground and injection-molded ('Van Dorn 110' at about 230°C stock temperature) into test specimens. The make-up of the composition and its properties are summarized in Table 4. A control is also summarized.

TABLE 4

Composition*	Control	Example 1
Himont Profax 6523 (PP)	100	87.5
Arco Dylark 332 (SMA)	---	10.0
Phillips K-Resin KR03 (SBR)	---	2.5
Properties		
Melt Flow g/10 min. (Cond. L)	4.5	4.1
Tensile Strength, psi	4990	5070
Flexural Modulus, psi	230,000	274,000
Flexural Strength, psi	7360	8490
Notched Izod Impact, ft.lb./in.	0.52	0.74
Gardner Impact, (RT) in.lb.	21	16
HDT at 66 psi, °C	84	104
Linear Shrinkage, in./in. %	1.6	1.3

* % by weight.

In addition, the molded specimens of Example 1 have excellent surface characteristics with respect to appearance and hardness.

Example 2

A blended polymer composition in accordance with the present invention is prepared on a Farrel Continuous Mixer (FCM), CP-23 at a mixer speed of 1000 rpm and extruded at about 220°C into strands which are passed through a water bath prior to pelletizing. The pellets are injection molded (220°C stock temperature and 30°C mold temperature) into test specimens. The makeup of the composition and its physical properties are summarized as follows:

TABLE 5

Composition	%/wt.
Shell 7C06 (PP copolymer)	52.45
Arco Dylark 332 (SMA)	20.00
Firestone Stereon 840A (SBR)	5.00
RT Vanderbilt Select-O-Sorb (talc)	20.00
CR-834 (TiO_2)	2.50
Ciba-Geigy Irganox 1010 (Stabilizer)	0.05
Properties	
Melt Flow, g/10 min.	2.0
Tensile Strength, psi	4036
Flexural Modulus, psi	373,000
Flexural Strength, psi	5967
Izod, Notched, ft.lb./in.	0.71
Izod, Unnotched, ft.lb./in.	8.40
Gardner Impact, in.lb.	27
HDT at 66 psi, °C	118
Linear Shrinkage, in./in. %	0.7

In addition to the high-heat distortion temperature and low shrinkage characteristics of the above compound, the molded specimens also exhibit high gloss and scratch resistant surface characteristics.

Example 3

A sheet is formed from the composition prepared in Example 2 on a 3.5-inch HPM extruder, with a two-stage screw of 30:1 L/D ratio and at a melt temperature of about 230°C. The extrudate is passed through polished rolls with a center roll temperature of about 94°C to form a sheet which is 48 inches wide. The sheet is cut into about 12-inch squares and the squares are then fed to a CAM thermoformer. When the squares are heated to their softening point, they are advanced to a forming

station where the squares are molded into the shape of a cup by a pressure-forming technique. The resulting cups are excellent in appearance and detail. The excellent thermoformability of the composition of Example 2 is similar to that obtained by commercial styrenics, and the talc-filled cups have superior gloss characteristics compared to a typically filled polypropylene compound.

Example 4

An extruded sheet prepared as in Example 3 with the composition of Example 2 is laminated on both sides with the polypropylene and/or a 20% talc-filled polypropylene sheet and subsequently thermoformed into cups in a single operation. The cups exhibit good adhesion between the layers of sheets, and the cups are of high quality.

Examples 5-9

Blends containing polypropylene, styrene maleic anhydride copolymer, talc and Phillips K-Resin KR03 (a multiblock copolymer) are prepared in a Banbury mixer (Farrel) at about 55°C and extruded at about 220°C into strands which are passed through a water bath prior to pelletizing. The pellets are injection-molded (220°C stock temperature) into test specimens. Table 6 identifies the various compositions of Examples 5-9 and a control sample identified as Control-2. Properties of these reinforced compositions also are listed in the table.

TABLE 6

		Example				
	Control-2	5	6	7	8	9
Exxon PD7132 (PP)	80	61	60	59	55	52
Jet Fil 500 (Talc)	20	20	20	20	20	20
Arco Dylark 332 (SMA)	--	15	15	15	18	20
Phillips K-Resin, KR03	--	4	5	6	7	8
Properties						
Melt Flow, g/10 min	1.9	1.8	1.7	1.9	1.9	2.0
Tensile Strength, psi	4060	4480	4410	4440	4570	4730
Tangent Modulus, Kpsi	287	340	341	345	346	338
Gardner Impact, in.lb.	35±10	7.5±2.5	9.2±3.6	8.3±2.2	11.2±6.2	10.4±3.3
HDT at 66 psi, °C	116	110	110	107	104	108
Linear Shrinkage, in/in %	1.09	0.65	0.71	0.59	0.59	0.61

As can be seen from the results summarized in Table 6, the blended compositions of the present invention exhibit superior linear shrinkage, modulus and tensile strength compared to Control Example 2.

Examples 10-12

Blended polymer compositions in accordance with the present invention are prepared utilizing the general procedure of Example 2 and with the components identified in the following Table 7. Examples 11 and 12 contain mixtures of two different compatibilizers and Example 12 also contains EVOH as a barrier polymer component. The properties of the blended polymer compositions of Examples 10-12 are summarized in Table 7.

TABLE 7

	Example		
	10	11	12
Shell 7C06 (PP copolymer)	75.45	65.45	43.95
Arco Dylark 332 (SMA)	9.60	9.60	14.50
Cain talc 4590 (talc)	10.00	10.00	15.00
White Pigment (TiO_2)	2.50	2.50	2.50
Irganox 1010 (Stabilizer)	0.05	0.05	0.05
Firestone Stereon 840A (SBR)	2.50	2.40	3.70
Shell Kraton G 1652 (SEBS)	---	10.00	10.00
EVOH Copolymer	---	---	10.00
Properties			
Melt Flow, g/10 min	1.5	1.5	1.0
Tensile Strength, psi	3840	3262	3265
Flexural Strength, psi	5334	4081	4477
Tangent Modulus, Kpsi	2.54	1.89	2.35
Izod, Notched, ft.lb./in.	1.07	2.4	0.75
Izod, Unnotched, ft.lb./in.	12.57	---	7.99
HDT at 66 psi, °C	93	89	92
Linear Shrinkage, in/in %	1.0	0.8	0.6

Example 13

A two-layer laminate is prepared in the following manner. A 40 mil sheet of the composition of Example 2 is prepared by extrusion. To this sheet of Example 2 there is heat laminated a 12 mil polypropylene cap layer (Shell 7C06). The original sheet prepared from the product of Example 2 and the two layer laminate are evaluated for impact strength in an Instrumented Impact Tester, (Rhemetrics Model RDT-5000). This test provides information on the amount of force (in pounds) required to rupture the test specimen at a certain preset velocity of a falling weight. The rating for the sheet prepared with the product of Example 2 is 64.7 pounds, and the value for the laminate is 144.2 pounds, a significant increase. Improved Gardner gloss also is observed. The Gardner gloss measured at a 60° angle. For the laminate, the Gardner reading is 61° on the Example 2 sheet side and 76° for the polypropylene side. In addition, taste and odor characteristics of the two-layer laminate is better with respect to the monolayer sheet.

Examples 14-15

These examples illustrate the use of a polyethylene/polypropylene mixture as the polyolefin in the compositions of the invention. The blends are prepared in accordance with the general procedure of Example 2 utilizing the ingredients and the amounts identified in Table 8. The properties of the blended polymer compositions thus obtained are also summarized in Table 8.

TABLE 8

Ingredients	Example 14	Example 15
Shell 7C06	52.5	47.4
Dylark 332	20.0	20.0
Stereon 840A	5.0	5.0
Cain (HDPE) 7030	---	5.0
Select-A-Sorb	20.0	20.0
TiO_2 (CR 834)	2.5	2.5
Properties		
Flexural Strength, psi	7310	7110
Flexural Modulus, Kpsi	391	357
HDT at 66 psi, °C	117	115
Gardner Impact, in.lb.	14	21
Shrinkage, in./in. %	0.65	0.59

The properties show improved impact for Example 15 without loss of other desirable properties.

Examples 16-18

These examples illustrate the use of multi-block, linear triblock and hydrogenated triblock copolymers. In this example, the blends are processed on a Leistritz counter-rotating, twin-screw, and injection molded. The types and amounts of polymers blended in these examples are summarized in the following Table 9. Some of the mechanical properties of the blended polymers also are summarized in the table.

TABLE 9

Ingredients	Example 16	Example 17	Example 18
Profax 6523	76	76	76
Dylark 332	19	19	19
Stereon 840A	5	--	--
Kraton D1102	--	5	--
Kraton G1652	--	--	5
Properties			
Flexural Modulus, Kpsi	280	264	247
Gardner Impact, in.lb.	17.4	4.2	4.0

The results summarized in Table 9 demonstrated the multi-block styrene butadiene copolymers provide better impact/modulus balance than the triblock copolymers.

Examples 19-20

These examples illustrate the use of impact-modified styrene maleic anhydride copolymers in the blended polymer compositions of the present invention. The blends were processed in accordance with the general procedure of Example 2 and molded. The composition of the formulations of these two examples and some of these properties are summarized in the following Table 10.

TABLE 10

Ingredients	Example 19	Example 20
Aristich 4040F[1]	52.4	52.4
Dylark 332	12.5	--
Dylark 238	--	12.5
Stereon 840A	12.5	12.5
Select-A-Sorb	20	20
TiO_2 (CR 834)	2.5	2.5
B-225[2]	0.1	0.1
Properties		
Flexural Modulus, Kspi	223	228
Izod Impact, notched (ft.lb./in.)	1.8	2.2
Gardner Impact, in.lbs.		
at RT	143	288
at -20°C	112	125
Linear Shrinkage, in./in., %	0.7	0.7

1 A polypropylene copolymer from Aristich.
2 A stabilizer from Ciba-Geigy.

Examples 21-22

These examples illustrate the use of another impact-modified styrene maleic anhydride copolymer in a formulation containing talc. A control formulation also is prepared which does not contain a compatibilizer. The blends are prepared on a Banbury mixer and injection molded (Van Dorn) by the general procedure of Example 1. The formulations and some of the properties obtained from the blended formulations are summarized in the following Table 11.

TABLE 11

Ingredients	Control-3	Example 21	Example 22
Exxon PD 7132 (PP)	60	57	55
Arco Arvyl 300 MR	20	20	20
Stereon 840	--	3	--
Jet Fill 500 (talc)	20	20	20
Phillips KR03	--	--	5
Properties			
Melt Flow, g/10 min (Cond. L)	1.4	1.0	1.3
Tensile Strength, psi	3460	3550	3810
Flexural Strength, psi	6300	6440	6870
Flexural Modulus, Kpsi	348	338	352
Notched Izod Impact ft.lb./in.	0.7	1.0	1.0
HDT at 66 psi, °C	115	110	106
Gardner Impact (RT) in.lbs.	5	21	23
Linear Shrinkage in./in. %	0.69	0.65	0.59

The above results demonstrate the improved impact strength obtained when compatibilizers in accordance with the present invention are included in the formulations.

Example 23

This example illustrates the use of a high-density polyethylene as the polyolefin. Control-4 does not contain the compatibilizer. The formulation of Example 23 and of Control-3, and some of the properties of the blended formulations are summarized in the following Table 12.

TABLE 12

Ingredients	Control-3	Example 23
Cain 7820	59.9	56.2
Cain 7040	20.0	18.7
Dylark 332	20.0	20.0
Stereon 840	--	5.0
B-225 Stabilizer	0.1	0.1
Properties		
Flexural Strength, psi	6764	6042
Flexural Modulus, Kpsi	214	203
HDT at 66 psi, °C	97	97
Gardner Impact (RT), in.lbs.	9	28
Linear Shrinkage in./in. %	1.34	1.27

The above results demonstrate the improved linear shrinkage and Gardner impact properties obtained when the compatibilizer is included in the blend.

Examples 24-25

These examples illustrate the use of functionalized block copolymers such as maleated styrene-butadiene-styrene triblock copolymers. The blends are prepared in a twin screw extruder and molded. The formulations of Examples 24 and 25 and some of the properties of the blends are summarized in the following Table 13.

TABLE 13

Ingredients	Example 24	Example 25
Profax 6523	85.5	85.5
Dylark 332	9.5	9.5
Kraton G1652	5	--
Kraton FG1901X	--	5
Properties		
Flexural Modulus, Kpsi	220	223
HDT at 66 psi, °C	96	109
Gardner Impact (RT) in.lb.	14.7	29

The above results demonstrate that the maleated triblock copolymer FG1901X provides improvements with respect to Gardner impact and HDT when compared to non-functionalized SBS.

Examples 26-27

These examples illustrate the use of Barex, a barrier resin in the formulations of the present invention. The polymer blend is prepared in a twin screw extruder and molded. The formulation and some of the properties of the blended formulation are summarized in the following Table 14.

TABLE 14

Ingredients	Control-5	Example 26	Example 27
Profax 6523	76	76	76
Dylark 332	19	19	19
Stereon 840A	--	3	5
Barex 210	5	2	--
Properties			
Flexural Modulus, Kpsi	282	251	235
Gardner Impact (RT) (in.lb.)	<2	8.0	11.6
Linear Shrinkage, in./in. %	1.07	1.10	1.11
Oxygen Permeation,*** $cc/m^2/day$	539*	593*	703**

* 8 mil sheet
** 7 mil sheet
*** at 0% relative humidity and 25°C

The above results demonstrate that the addition of a small amount of Barex of the composition of this invention (Example 26) significantly improves the oxygen impermeability.

Foams of the blended polymer compositions of the present invention may be prepared by mixing low boiling foaming agents with the blended polymer compositions at a temperature above the softening point of the polymer temperature and under a pressure which prevents foaming of the mixture, followed by extrusion of the foamable mixture into a zone of lower pressure wherein the foamable mixture foams to provide the desired foamed body. Particularly suitable foaming agents include halohydrocarbons containing 1 or 2 carbon atoms such as methyl chloride, ethyl chloride, etc. Low boiling hydrocarbons also are suitable, and these include propane,

butane, pentane, etc. Mixtures of the above described blowing agents also can be used. The amount of blowing agent included in the foamable compositions is from about 5 to about 30% by weight based on the total weight of the blended polymer composition of the invention. The foamed articles prepared in this manner may be semi-rigid to rigid foams having densities of from 10 to about 200 g/l. By varying the temperature during extrusion of the foamable mixture, and by varying the expanding agent used, the foams produced have varying properties of open and closed cells. The foams are particularly useful in the building industry and as insulation.

Other uses for the blended polymer compositions of this invention include refrigeration parts such as inner liners, inner door panels, inner gaskets and trim, trays and shelves, etc. The blended polymers are useful in preparing parts for: the automotive industry; communications such as telephones, ratio, TV, cassettes, etc.; power tools; appliances; business machines; toys; furniture; etc. The properties of the blended polymer compositions of this invention can be varied to satisfy the requirements of these different applications.

While the invention has been described and illustrated with reference to certain preferred embodiments thereof, those skilled in the art will appreciate that various changes, modifications and substitutions can be made therein without departing from the spirit of the invention. For example, processing and molding techniques other than those preferred as set forth hereinabove may be applicable due to variations in the desired end product and uses, etc. Moreover, the specific results observed with respect to the physical properties

may vary depending on the specific polymers and formulations selected and whether same are used alone or in combination with each other, i.e., mixture, or other known agents. Accordingly, such expected changes and variations in results are contemplated in accordance with the objects and practices of the present invention. It is intended therefore, that the invention be limited only by the scope of the claims which follow.

Claims

1. A blended polymer composition comprising

(A) at least one olefin polymer;

(B) at least one polymer characterized as having a glass transition temperature above the glass temperature of olefin polymer (A) and selected from the group consisting of

(B-1) copolymers of a vinyl aromatic compound and an unsaturated dicarboxylic acid anhydride, imide, metal salt, or partial ester of said dicarboxylic acids, or mixtures thereof;

(B-2) terpolymers comprising a vinyl aromatic compound and an unsaturated dicarboxylic acid anhydride, imide, metal salt or partial ester of said dicarboxylic acids or mixtures thereof, and a copolymerizable monomer;

(B-3) blends or reaction products of elastomers and the copolymer of (B-1) or terpolymer of (B-2);

(B-4) blends comprising a polymer of a vinyl aromatic compound and a polyarylene ether, and optionally an elastomer;

(B-5) copolymers and terpolymers of a vinyl aromatic compound with an acrylic ester and/or an alkyl-substituted acrylic ester;

(B-6) product of the reaction of an alpha,beta-olefinically unsaturated carboxylic reagent and a hydrogenated block copolymer of a vinyl aromatic compound and an aliphatic conjugated diene; and

(B-7) polycarbonates;

(B-8) graft copolymers of a monoethylenically unsaturated resin-forming monomer and a terpolymer of two different alpha-mono-olefins and a non-conjugated diene;

(B-9) acrylic polymers;

(B-10) nitrile resins; and

(B-11) acrylic-styrene-acrylonitrile polymers;

(B-12) acrylonitrile-halogenated polyolefin-styrene terpolymers and mixtures of two or more of (B-1) to (B-12);

(C) an effective amount of a compatibilizing agent selected from the group consisting of diblock, triblock, multiblock, starblock or graftblock copolymers of a vinyl aromatic compound and a conjugated diene or the partially hydrogenated derivatives thereof, and mixtures thereof.

2. The polymer composition of claim 1 wherein the compatibilizing agent (C) is at least one multi-block, starblock or graftblock copolymer.

3. The polymer composition of claim 1 wherein the olefin polymer (A) is selected from the group consisting of olefin homopolymers, olefin copolymers and mixtures thereof.

4. The polymer composition of claim 1 wherein the olefin polymer (A) is a polymer of an alpha-olefin containing from 2 to about 6 carbon atoms.

5. The polymer composition of claim 1 wherein the olefin polymer (A) is polyethylene, polypropylene, or mixtures thereof.

6. The polymer composition of claim 1 wherein the polymer (B) is (B-1), a copolymer of a styrene and a maleic anhydride or an N-hydrocarbyl-substituted male-imide.

7. The polymer composition of claim 1 wherein the polymer (B) is (B-4), polystyrene blended with a polyarylene ether and an elastomer.

8. The polymer composition of claim 7 wherein the polyarylene ether is a polyphenylene ether.

9. The polymer composition of claim 1 wherein the compatibilizing agent (C) is a multiblock copolymer of styrene and butadiene, styrene and isoprene, partially hydrogenated derivatives thereof, or mixtures thereof.

10. The polymer composition of claim 9 wherein the compatibilizing agent comprises at least about 40% by weight of styrene.

11. The polymer composition of claim 9 wherein the multiblock copolymer comprises from about 40% to about 75% by weight of styrene.

12. The polymer composition of claim 1 also containing

(D) at least one resin having low gas and vapor transmission properties.

13. The polymer composition of claim 12 wherein the resin (D) is selected from the group of resins consisting of vinylidene chloride polymers and copolymers, copolymers of ethylene and vinyl alcohol, polyamides; and nitrile resins derived from alpha,beta-olefinically unsaturated nitriles.

14. The polymer composition of claim 1 also containing

(E) at least one filler, fiber, or mixtures thereof.

15. The polymer composition of claim 14 wherein the filler is talc or calcium carbonate, and the fiber is glass fiber.

16. A blended polymer composition comprising

(A) from 1 to about 99% by weight of at least one alpha-olefin polymer;

(B) from 1 to about 99% by weight of at least one polymer characterized as having a glass transition temperature above the glass temperature of olefin polymer (A) and selected from the group consisting of

(B-1) copolymers of a vinyl aromatic compound and an unsaturated dicarboxylic acid anhydride or imide, or mixtures thereof;

(B-2) terpolymers comprising a vinyl aromatic compound and an unsaturated dicarboxylic acid anhydride or imide, or mixtures thereof, and a copolymerizable monomer;

(B-3) blends or reaction products of elastomers and the copolymer of (B-1) or terpolymer of (B-2);

(B-4) blends comprising a polymer of a vinyl aromatic compound and a polyarylene ether, and optionally an elastomer;

(B-5) copolymers and terpolymers of a vinyl aromatic compound with an acrylic ester and/or an alkyl-substituted acrylic ester;

(B-6) product of the reaction of an alpha,beta-olefinically unsaturated carboxylic reagent and a hydrogenated block copolymer of a vinyl aromatic compound and an aliphatic conjugated diene; and

(B-7) polycarbonates;

(B-8) graft copolymers of a monoethylenically unsaturated resin-forming monomer and a terpolymer of two different alpha olefins and a non-conjugated diene;

(B-9) acrylic polymers;

(B-10) nitrile resins;

(B-11) acrylic-styrene-acrylonitrile polymers; and

(B-12) acrylonitrile-halogenated polyolefin-styrene polymers, or mixtures of two or more of (B-1) to (B-12); and

(C) from about 1 to about 40% by weight of at least one compatibilizing agent selected from the group consisting of diblock, triblock, multiblock, or graft-block copolymers of a vinyl aromatic compound and a conjugated diene, or the partially hydrogenated derivatives thereof, and mixtures thereof.

17. The polymer composition of claim 16 wherein the olefin polymer of (A) is polyethylene, polypropylene or mixtures or copolymers thereof.

18. The polymer composition of claim 16 wherein the polymer (B) is polymer (B-1) a copolymer of styrene and maleic anhydride or (B-2) a terpolymer comprising styrene, maleic anhydride, and an acrylic ester or alkyl-substituted acrylic ester, or (B-3) blends or reaction products of elastomers and the copolymer (B-1) or terpolymer (B-2).

19. The polymer composition of claim 16 wherein the polymer (B) is (B-4), a blend of a vinyl aromatic compound, a polyphenylene ether and an elastomer.

20. The polymer composition of claim 19 wherein the elastomer is a polymer of a conjugated diene.

21. The polymer composition of claim 16 wherein the compatibilizing agent (C) is a multiblock copolymer of styrene and butadiene, styrene and isoprene, or the partially hydrogenated derivatives thereof.

22. The polymer composition of claim 16 comprising from about 45% by weight to about 90% by weight of the polyolefin (A) and from about 10% to about 30% by weight of a copolymer of styrene and maleic anhydride (B).

23. The polymer composition of claim 16 also containing

(D) from about 0.5 to about 20% by weight of at least one resin having low gas and vapor transmission properties and selected from the group consisting of vinylidene chloride polymers and copolymers, copolymers of ethylene and vinyl alcohol, polyamides; and nitrile resins derived from alpha,beta-olefinically unsaturated mononitriles.

24. The polymer composition of claim 16 wherein the polymer (B) is characterized as having a glass transition temperature above about 75°C.

25. The polymer composition of claim 23 wherein (D) is an acrylonitrile based resin containing at least 65% of an acrylonitrile.

26. The polymer composition of claim 16 also containing

(E) at least one filler, fiber, or mixtures thereof.

27. The polymer composition of claim 26 wherein the filler (E) is talc or calcium carbonate, and the fiber is a glass fiber.

28. A polymer composition comprising

(A) from about 49% by weight to about 90% by weight of polypropylene;

(B) from about 10% to about 30% by weight of a copolymer of styrene and maleic anhydride;

(C) from about 2% to about 10% by weight of a starblock or multiblock copolymer of styrene and butadiene, styrene and isoprene, their hydrogenated derivatives or mixtures thereof; and

(E) the balance of talc or calcium carbonate.

29. A polymer composition comprising

(A) from about 50% to about 52% by weight of polypropylene;

(B) from about 18% to about 20% by weight of a copolymer of styrene and maleic anhydride;

(C) from about 5% to about 7% by weight of a starblock, multiblock, or diblock copolymer of styrene and butadiene, or mixtures thereof;

(D) from 0% to about 5% by weight of a triblock copolymer of styrene and butadiene; and

(E) about 20% by weight of talc.

30. A thermoformable multilayer structure comprising

(I) at least one layer of a blended polymer composition according to claim 1; and

(II) at least one layer of an olefin polymer composition.

31. The thermoformable multilayer structure of claim 30 wherein the layer of olefin polymer composition is a layer of polyethylene or polypropylene or their copolymers.

32. A thermoformable multilayer structure comprising

(I) at least one layer of a blended polymer composition according to claim 16; and

(II) at least one layer of an olefin polymer composition.

33. The thermoformable multilayer structure of claim 32 wherein the layer of olefin polymer composition is a layer of polyethylene or polypropylene.

34. A thermoformable multilayer structure comprising

(I) at least one layer of a blended polymer composition according to claim 1; and

(II) at least one layer of a barrier polymer composition.

35. The thermoformable multilayer structure of claim 34 wherein the layer of barrier polymer (II) is applied from a solution or dispersion of the barrier polymer in an organic liquid or water.

36. A thermoformable multilayer structure comprising

(I) at least one layer of a blended polymer composition according to claim 1; and

(II) at least one layer of an aromatic or aliphatic vinyl polymer.

37. The thermoformable multilayer structure of claim 36 wherein the layer of vinyl polymer (II) is applied from a solution or dispersion of the vinyl polymer in an organic liquid or water.

38. A molded article having a desired shape produced from the blended polymer composition according to claim 1.

39. A molded article having a desired shape produced from a blended polymer composition according to claim 16.

40. A molded article having a desired shape prepared by the process comprising

(A) feeding a sheet of the blended polymer composition of claim 1 to a heating station;

(B) heating said sheet to its softening point; and

(C) feeding the softened sheet to a forming station where it is molded into molded articles of the desired shape.

41. A shaped article prepared by extrusion, coextrusion, thermoforming, blow molding, injection

molding, compression molding, laminating, calendering, stamping, pultrusion, foaming, or extrusion die coating onto continuous fibers, the polymer composition of claim 1.

42. A shaped article prepared by extrusion, coextrusion, thermoforming, blow molding, injection molding, compression molding, laminating, calendering, stamping, pultrusion, foaming, or die coating onto continuous fibers, the polymer composition of claim 16.

43. A coextruded multilayer structure wherein at least one layer comprises the composition of claim 1.

44. A coextruded multilayer structure wherein at least one layer comprises the composition of claim 16.

45. The coextruded multilayer structure of claim 43 wherein at least one additional layer comprises polyethylene or polypropylene.

46. The polymer composition according to claim 1 wherein said composition further comprises a scrap material comprising the same composition obtained from a preceding molding operation using the polymer composition of claim 1.

47. A thermoformable multilayer structure comprising

(I) at least one layer of the polymer composition of claim 46; and

(II) at least one layer of the blended polymer composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04815

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5] C08K 3/26,40; C08L 31/02; 33/00; 37/00; 39/04; 51/04; 53/00

U.S. CL. 524/425,451; 525/70,71,73,74,78,80,92

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S. CL	524/425,451; 525/70,71,73,74,78,80,92

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4,110,303 (GERGEN et al) 29 AUGUST 1978 (note cols 1.2,5,6,25	1-6,9-18,21,22, 24,38-42,46
Y	US, A, 4,269,950 (ABOLINS et al) 26 MAY 1981 (note cols 2 and 7)	1-6,9-18,21,22, 24,38-42 & 46
Y	US, A, 4,501,843 (NEEDHAM) 26 FEBRUARY 1985 (note col.2)	15

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
09 MARCH 1990	26 MAR 1991
International Searching Authority	**Signature of Authorized Officer**
ISA/US	J. ZIEGLER

International Application No. PCT/US89/04815

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE[1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter[12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out[13], specifically:

3. ☐ Claim numbers ________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING[2]

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Components A, B is (B-1) and (B-2) as recited and C, classified in Class 525, subclass 63+.

II. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Group I components wherein B is B-3 as recited, classified in Class 525, subclass 63+.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

   1-6, 9-18, 21, 22, 24, 38-42 and 46

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Cotinuation
Observations where Unity of Invention is lacking International Application No PCT/US89/04815

FURTHER INFORMATION CONTINUED FROM THE FIRST SHEET
(Not for publication)

III. Claim 7, 8, 19 and 20, drawn to Group I components wherein B is (B-4) as recited, classified in Class 525, subclass 68+.

IV. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Group I components when B is (B-5), classified in Class 525, subclass 63+.

V. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Group I components when B is (B-6), classified in Class 525, subclass 63+.

VI. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Group I components when B is (B-7), classified in Class 525, subclass 67.

VII. Claims 1-6, 9-18, 21, 22, 24, 38-42 and 46, drawn to Group I components when B is (B-8), classified in Class 525, subclass 63+.

VII. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46 drawn to Group I components when B is (B-9), (B-10) or (B-11), classified in Class 525, subclass 63+.

VIII/IX. Claims 1-6, 9-18, 21, 22, 24, 38-42, 46, drawn to Group I components when B is B-12, classified in Class 525, subclass 63+.

X. Claims 12, 13, 23, 25, drawn to Group I components plus D as recited, classified in Class 525, subclass 60+.

XI. Claims 12, 13, 23, 25, drawn to Group II plus Component D, classified in Class 525, subclass 60+.

XII. Claims 12, 13, 23, 25, drawn to Group III plus D, classified in Class 525, subclass 60+.

XIII. Claims 12, 13, 23, 25, drawn to Group IV plus D, classified in Class 525, subclass 60+.

XIV . Claims 12, 13, 23 and 25, drawn to group V plus D, classified in Class 525, subclass 60+.

XV . Claims 12, 13, 23 and 25, drawn to group VI plus D, classified in Class 525, subclass 60+.

XVI . Claims 12, 13, 23, 25, drawn to Group VII plus D, classified in Class 525, subclass 60+.

XVII . Claims 12, 13, 23, 25, drawn to Group VIII plus D, classified in Class 525, subclass 60+.

XVIII. Claims 12, 13, 23, 25, drawn to Group IX plus D, classified in Class 525, subclass 60+.

XIX. Claims 14, 15, 26-29, drawn to Group I plus component E, classified in Class 524, subclass 425+.

XX. Claims 14, 15, 26-29, drawn to Group II plus E, classified in Class 524, subclass 425+.

XXI. Claims 14, 15, 26-29, drawn to Group III plus E, classified in Class 524, subclass 425+.

XXII. Claims 14, 15, 26-29, drawn to Group IV plus E, classified in Class 524, subclass 425+.

XXIII. Claims 14, 15, 26-29, drawn to group V plus E, classified in Class 524, subclass 425+.

XXIV. Claims 14, 15, 26-29, drawn to Group VI plus E, classified in Class 524, subclass 425+.

XXV. Claims 14, 15, 26-29, drawn to Group VII plus E, classified in Class 524, subclass 425+.

XXVI. Claims 14, 15, 26-29, drawn to Group VIII plus E, classified in Class 524, subclass 425+.

XXVII. Claims 14, 15, 26-29, drawn to Group IX plus E, classified in Class 524, subclass 425+.

XXVIII. Claims 30-33, drawn to multilayered structure having Group I plus layer of olefin polymer, classified in Class 428, subclass 412+; 500+.

XXIX. Claims Group XXVIII structure wherein Group I is Group II components, drawn to 428, classified in Class 428, subclass 412+; 500+.

XXX. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group III components, classified in Class 428, subclass 412+, 500+.

XXXI. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group IV components, classified in Class 428, subclass 412+, 500+.

XXXII. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group V components, classified in Class 428, subclass 412+; 500+.

XXXIII. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group VI components, classified in Class 428, subclass 412+, 500+.

XXXIV. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group VII components, classified in Class 428, subclass 412+, 500+.

XXXV. Claims 30-33, drawn to Group XXVIII structure wherein Group I is Group VIII components, classified in Class 428, subclass 412+; 500+.

XXXVI. Claims 30-33, drawn to Group XXXVIII structure wherein Group I is Group IX components classified in Class 428, subclass 412; 500+.

XXXVII. Claims 30-33, drawn to multilayer structure having Group 1 plus barrier layer, classified in Class 428, subclass 412+; 500+.

XXXVIII. Claims 34, 35 multilayer structure having group I plus barrier layer, drawn to 428, classified in Class 428, subclass 412+; 500+.

XXXIX. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group II, classified in Class 412, subclass 412+; 500+.

XL. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group III, classified in Class 428, subclass 412+; 500+.

XLI. Claims 34, 35, drawn to Group XXXVIII structure wherein Group 1 is Group IV, classified in Class 428, subclass 412+; 500+.

XLII. Claims 34, 35, drawn to Group XXXVIII structure wherein Group 1 is Group V, classified in Class 428, subclass 412+; 500+.

XLIII. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group VI, classified in Class 428, subclass 412+; 500+.

XLIV. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group VII, classified in Class 428, subclass 412; 500+.

XLV. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group VIII, classified in Class 428, subclass 412+; 500+.

XLVI. Claims 34, 35, drawn to Group XXXVIII structure wherein Group I is Group IX, classified in Class 428, subclass 412+; 500+.

XLVII. Claims 36, 37, drawn to multilayered structure having Group I plus aromatic or aliphatic vinyl polymer, classified in Class 428, subclass 412+; 500+.

XLVIII. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group II, classified in Class 428, subclass 412+; 500+.

XLVIX. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group III, classified in Class 428, subclass 412+; 500+.

L. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group IV, classified in Class 428, subclass 412+; 500+.

LI. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group V, classified in Class 428, subclass 412+, 500+.

LII. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group VI, classified in Class 428, subclass 412+, 500+.

LIII Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group VII, classified in Class 428, subclass 412+; 500+.

LIV. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group VIII, classified in Class 428, subclass 412+; 500+.

LV. Claims 36, 37, drawn to Group XLVII structure wherein Group I is Group IX, classified in Class 428, subclass 412+; 500+.

LVI. Claim 47, drawn to multilayer structure of (1) layer, as recited and (11) Group I components, classified in Class 428, subclass 412+; 500+.

LVII. Claim 47, drawn to Group LVI structure wherein (11) is Group II, classified in Class 428, subclass 412+; 500+.

LVIII. Claim 47, drawn to Group LVI structure wherein (11) is Group III, classified in Class 428, subclass 412+; 500+.

LIX. Claim 47, drawn to Group LVI structure wherein (11) is Group IV, classified in Class 428, subclass 412; 500+.

LX. Claim 47, drawn to Group LVI structure wherein (11) is Group V, classified in Class 428, subclass 412+; 500+.

LXI. Claim 47, drawn to Group LVI structure wherein (11) is Group VI, classified in Class 428, subclass 412+; 500+.

LXII. Claim 47, drawn to Group LVI structure (11) is Group VII, classified in Class 428, subclass 412+; 500+.

LXIII. Claim 47, drawn to Group LVI structure wherein (11) is Group VIII, classified in Class 428, subclass 412+; 500+.

LXIV. Claim 47, drawn to Group LVI structure wherein (11) is Group IX, classified in Class 428, subclass 412+; 500+.

The above inventions Group I through and including Group LXIII lack unity under PCT Rule 13 since:

1) Group I can be used as a molding composition, per se, other than B being (B-4) or other enumerated B's as defined in Groups II to IX.

2) Groups I to IX can be used as molding composition without the presence of (a) Component D (Groups X to XVIII or (b) Component E (Groups XIX to XXVII.

3) Groups I-IX can be used as a molding composition per se not requiring to be (a) the structure of Group XXVIII to XXXVII plus layer of olefin polymer; (b) structure of Groups XXXVIII to XLVI plus barrier

layer; (c) structure of Groups XLVII to LV plus layer of aromatic or aliphatic vinyl polymer or (d) the structure of Groups LVI to LXIV of layer (1) plus Group I components,

(4) The structure of Groups XXVIII to XXXVII plus layer of olefin polymer is not the structure of (a) Groups XXXVIII to XLVI plus the barrier layer, (b) Groups XLVII to LV plus layer of aromatic or vinyl polymer or (C) the structure of Groups LVI to LXIII of layer (1) plus Group I components.